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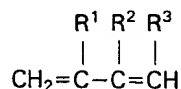
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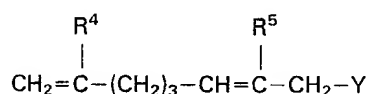
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(54) Catalytic process for alkatrienols and derivatives

(57) A method for the preparation of unsaturated compounds containing at least 12 carbon atoms which comprises reacting a 1,3-diene of the formula:



wherein each of R¹ and R², independently, represents hydrogen or alkyl and R³ represents hydrogen, alkyl or alkenyl, with a 1-substituted-2,7-alkadiene of the formula:



wherein each of R⁴ and R⁵ independently, represents hydrogen or alkyl, Y represents a hydroxy, alkoxy, cycloalkoxy, aryloxy or acyloxy radical, in the presence of a rhodium compound and a chromium halide.

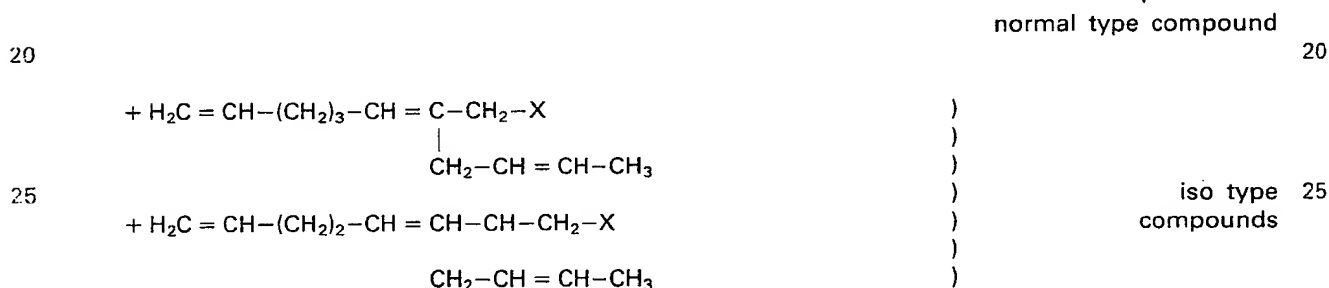
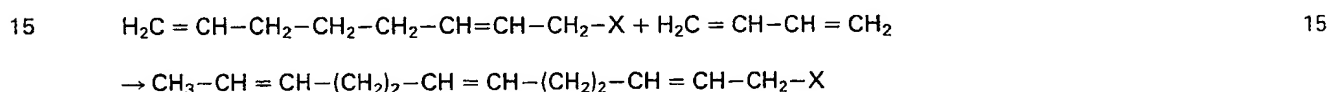
The products are useful intermediates in the manufacture of detergents.

SPECIFICATION

Chemical process

5 This invention relates to a chemical process and more particularly to a method for the preparation of certain 5
unsaturated compounds.

It is already known from United Kingdom Patent Specification No. 1316725 to prepare unsaturated
compounds having the structure of oligomers of butadiene by reacting a conjugated diene with a
1-substituted-2,7-alkadiene in the presence of a rhodium compound as catalyst. The reaction product
10 contains a mixture of a straight chain compound which has been referred to as a "normal type compound" 10
and branched chain compounds which have been referred to as "iso type compounds". Thus, the reaction
between 1,3-butadiene and a 1-substituted-2,7-octadiene may be represented as follows:



30 The ratio of normal type compound to iso type compounds will be referred to as the n/iso ratio. 30

The substituent X in the above compounds can be a hydroxy, alkoxy, aryloxy or acyloxy group.

The products of the reaction are useful chemical intermediates. In particular, the acyloxy substituted
products may be converted by hydrolysis and hydrogenation into saturated higher alcohols useful in the
35 manufacture of surfactant materials. 35

Methods for enhancing the activity of the rhodium catalyst have been proposed. Thus, Japanese Patent
Publication No. 75-13767 describes a process in which carbon tetrachloride or an alkylsilicon chloride is used
in addition to the rhodium compound. According to Japanese Patent Publication No. 77-38533, the activity of
this catalyst/co-catalyst system may be further improved by carrying out the reaction in the presence of
40 hydrogen. 40

It has now been found that the reaction can be carried out extremely efficiently if the reaction mixture
contains a chromium halide in addition to the rhodium compound.

Thus, according to the invention, there is provided a method for the preparation of unsaturated
compounds containing at least 12 carbon atoms which comprises reacting a 1,3-diene of the formula:



50 wherein each of R¹ and R², independently, represents hydrogen or alkyl and R³ represents hydrogen, alkyl or 50
alkenyl, with a 1-substituted-2,7-alkadiene of the formula:

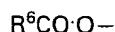


wherein each of R⁴ and R⁵, independently, represents hydrogen or alkyl and Y represents a hydroxy, alkoxy,
30 cycloalkoxy, aryloxy or acyloxy radical, in the presence of a rhodium compound and a chromium halide. 30

The alkyl radicals which may be represented by R¹ to R⁵ are preferably lower alkyl (C₁-C₄) radicals. Alkenyl
radicals which may be represented by R³ preferably contain from two to four carbon atoms.

Alkoxy radicals which may be represented by Y include, in particular, lower alkoxy radicals.

Suitable aryloxy radicals include phenoxy and alkyl substituted phenoxy radicals. Suitable acyloxy
35 radicals include radicals of the formula: 35



wherein R^6 represents an optionally substituted alkyl (especially lower alkyl), aralkyl, cycloalkyl or aryl radical.

5 As examples of 1,3-dienes which may be used in the method of the invention, there may be mentioned isoprene, piperylene, 1,3,7-octatriene and especially 1,3-butadiene.

Substituted alkadienes for use in the method of the invention may be prepared by methods that have been fully described in the prior art. Thus, reaction of 1,3-butadiene with a carboxylic acid in the presence of a catalyst comprising palladium acetate and triarylphosphine or triaryl phosphite gives the corresponding 10 1-acyloxy-2,7-octadiene with some 3-acyloxy-1,7-octadiene. For use in the method of the invention, 1-acetoxy-2,7-octadiene is a particularly preferred component.

The rhodium compound employed in the method of the invention may be an inorganic or organic salt or an organic complex. Examples of such compounds include rhodium trichloride, rhodium tribromide, rhodium nitrate, rhodium acetate, tetrakis(π -allyl)dichlorodirrhodium, tetrakis(ethylene)dichlorodirrhodium, 15 bis(cycloocta-1,5-diene)dichlorodirrhodium and bis(π -crotyl)tetrachloro(butadiene)dirrhodium. The preferred catalyst is rhodium trichloride. The rhodium compound may be added directly to the other components of the reaction mixture but is preferably used in the form of a solution in an alcohol such as ethanol or in a hydrocarbon such as toluene. Suitable amounts of rhodium compound are in the range 10^{-7} to 10^{-1} gram-atom rhodium per mole of alkadiene.

20 The chromium halide used in the method of the invention is preferably a chloride such as $CrCl_3 \cdot 6H_2O$ or $CrCl_3 \cdot 3THF$ (THF is tetrahydrofuran) or a corresponding bromide. Suitable amounts of chromium halide are in the range 10^{-5} to 0.5 m.mol per mole of alkadiene.

The method of the invention may be performed by carrying out the reaction in a suitable reactor, for example an autoclave, at a temperature in the range 50° - $250^\circ C$, preferably 100° - $130^\circ C$. The reaction may 25 take place under autogenous pressure and the reactants may be used in bulk or in the form of solutions in suitable solvents.

The reaction may be further promoted by hydrogen gas. Thus, it is advantageous to carry out the reaction in the presence of hydrogen at a pressure of 0.1 to 100 atmospheres, preferably 10 to 15 atmospheres.

30 The products obtained by the method of the invention are useful as chemical intermediates. In particular, those products containing hydroxyl groups, or groups convertible to hydroxyls such as acyloxy groups, are useful in the manufacture of detergents and other surfactant materials.

The invention is illustrated but not limited by the following Examples. The acetoxyoctadiene used in Examples 1-4 was a mixture consisting of 95% 1-acetoxy-2,7-octadiene and 5% 3-acetoxy-1,7-octadiene.

35 Example 1

To 7.10 g (42.2 mmol) acetoxyoctadiene in a strong-walled glass reactor vessel with pressure resistant PTFE valve were added 0.001 mmol of bis(π -crotyl)tetrachloro(butadiene)dirrhodium (complex A) in 0.2 ml toluene (0.002 mg-atom Rh) and 0.1g $CrCl_3 \cdot 6H_2O$. The mixture was cooled to $-20^\circ C$ and 1,3-butadiene (6 ml) was condensed in. The vessel was sealed and heated for 1 hour on an oilbath at $107^\circ C$ with magnetic stirring.

40 G.l.c. analysis and mass spectrometry showed that the reaction products consisted mainly of the normal and the iso type isomers of $C_{12}H_{19}OOCCH_3$. The products were further identified by their known n.m.r. spectra. The conversion of acetoxyoctadiene was 22.3% the selectivity to n- and iso- $C_{12}H_{19}OAc$ compounds 100% and the n/iso ratio 1.3. The turnover number, taken as a measure of catalytic activity and expressed in moles converted acetoxyoctadiene per g-atom Rh per hour, was 4700.

45 Example 2

The same method for Example 1 was followed for reacting acetoxyoctadiene with butadiene (4 ml) in the presence of 0.002 mmol $RhCl_3$ in 0.2 ml ethanol and of $CrCl_3 \cdot 6H_2O$ in various amounts. The mixture was heated for 1 hour at $110^\circ C$. The results are collected in Table 1.

TABLE 1

Run No.	Acetoxy-octadiene (mmol)	$CrCl_3 \cdot 6H_2O$ (mg)	Conv. (%)	sel. (%)	n/iso ratio	turnover number
1	42.0	3	8	100	1.3	1760
2	42.3	20	22	99	1.2	4570
3	41.9	100	54	97	1.2	6410

Example 3

50 The same method as in Example 1 was employed for reacting 8.42 g (50.08 mmol) acetoxyoctadiene with 9 t-5

ml butadiene in the presence of 0.0005 mmol complex A in 0.1 ml toluene and 1.0 g $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ at 110°C . After 105 minutes, 34% of the acetoxyoctadiene was converted to C_{12} acetate isomers in 98% selectivity, the n/iso ratio was 1.3 and the turnover number was 9730.

5 Example 4

Liquefied butadiene (9 ml, ca. 100 mmol) was added at -20°C to 8.41 g (50.0 mmol) acetoxyoctadiene. A solution of 0.0005 mmol Complex A in 0.1 ml toluene (0.001 mg-atom Rh), 0.90 g n-dodecane (g.l.c. standard) and 0.5 g $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were added. The mixture was heated for 2 hours at 120°C in a glass-lined stainless steel autoclave under 150 psi H_2 pressure and stirred magnetically. G.l.c. analysis after venting showed that 42% of the acetoxy-octadiene was converted to C_{12} acetate isomers in 97% selectivity (n/iso = 1.2). The turnover number was 10500.

Example 5

The same method as in Example 1 was followed for reacting 4.05 g (20.0 mmol) 1-phenoxy-2,7-octadiene with butadiene (4 ml, 46 mmol) in the presence of 0.01 mmol RhCl_3 in 1 ml ethanol, 0.38 g n-pentadecane (g.l.c. standard) and 0.5 g $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ at 110°C for 1 hour. The conversion was 24.3%, the selectivity to C_{12} phenoxides 99%, the n/iso ratio 0.8 and the turnover number 490.

CLAIMS

1. A method for the preparation of unsaturated compounds containing at least 12 carbon atoms which comprises reacting a 1,3-diene of the formula:



wherein each of R^1 and R^2 , independently, represents hydrogen or alkyl and R^3 represents hydrogen, alkyl or alkenyl, with a 1-substituted-2,7-alkadiene of the formula:



wherein each of R^4 and R^5 independently, represents hydrogen or alkyl, Y represents a hydroxy, alkoxy, cycloalkoxy, aryloxy or acyloxy radical, in the presence of a rhodium compound and a chromium halide.

2. A method according to claim 1 substantially as hereinbefore described with reference to the foregoing Examples.